

Investigation of the $F + H_2$ transition state region via photoelectron spectroscopy of the FH_2^- anion

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The $F + H_2$ reaction is one of the most important model systems in the development of state-to-state chemistry. Many asymptotic features of this reaction have been well characterized, including the rate constant at several temperatures,¹⁻⁴ the HF product vibrational branching ratio,⁵⁻⁸ and product state-resolved differential cross sections.⁹ In recent years, considerable theoretical effort has been devoted towards the development of *ab initio* potential energy surfaces for the reaction.¹⁰⁻¹⁴ A series of state-of-the-art scattering calculations¹⁵⁻²⁰ has been performed on one of these surfaces, the T5a surface developed by Steckler *et al.*¹⁰ However, while the experimental results⁵⁻⁹ have firmly established the HF($v = 2$) is the dominant product vibrational channel, the scattering calculations on the T5a potential energy surface predict HF($v = 3$) to be the dominant channel. (References 15-18 are restricted to $J = 0$, but Refs. 19 and 20 sum over several partial waves.) This indicates that additional work on the $F + H_2$ surface is required.

In order to gain further insight into the $F + H_2$ potential energy surface, we have measured the photoelectron spectrum of the FH_2^- anion. Previously, we have shown that photodetachment of a stable negative ion can probe the transition state region of a neutral bimolecular reaction, provided that the ion geometry is close to that of the neutral transition state.²¹⁻²³ A recent *ab initio* calculation by Simons²⁴ shows that the equilibrium geometry of FH_2^- is quite close to the FH_2 saddle-point geometry on the T5a surface. Thus, even though the binding energy of the anion is predicted²⁴ to be relatively weak [$D_0 = 0.17$ eV, relative to $F^- + H_2(v = 0)$], one obtains reasonable geometric overlap with the neutral transition state region because the barrier for the reaction lies in the $F + H_2$ entrance valley.

The experiments were performed on a negative ion time-of-flight photoelectron spectrometer described in detail previously.²¹ FH_2^- is formed by expanding a mixture of 5% NF_3 in H_2 through a pulsed molecular beam valve and crossing the molecular beam with a 1 keV electron beam just outside the valve orifice. Negative ions are extracted from the beam with a pulsed electric field and pass through a time-of-flight mass spectrometer.²⁵ The mass-selected ions are photodetached with the fourth harmonic of a Nd:YAG laser (266 nm, 20 Hz repetition rate), and a small fraction (10^{-4}) of the ejected photoelectrons is energy-analyzed by time of flight. The instrumental resolution is 8 meV at an electron kinetic energy (eKE) of 0.65 eV and degrades as $(eKE)^{3/2}$.

Figure 1 shows the experimental photoelectron spectrum of FH_2^- resulting from 400 000 laser shots. The spec-

trum shows a few small peaks on top of a broad background. Assuming the ion is in its ground state, the electron kinetic energy, eKE, is given by

$$eKE = h\nu - D_0 - EA(F) - E^{(0)} \quad (1)$$

Here $h\nu = 4.66$ eV is the photon energy and $EA(F)$ is the electron affinity of fluorine (3.40 eV). $E^{(0)}$ is the internal energy of the neutral FH_2 complex relative to $F + H_2(v = 0)$. Hence, $eKE(\text{eV}) = 1.09 - E^{(0)}$. The FH_2^- spectrum is quite different from that of F^- (top of Fig. 1) and indicates that the F atom interacts strongly with H_2 in the geometry probed by photodetachment of FH_2^- . This is consistent with our expectation that the geometry of the ion and neutral transition state are similar. The two small highest energy peaks in the FH_2^- spectrum correspond exactly to the two peaks in the F^- photoelectron spectrum; these peaks most likely result from dissociation of FH_2^- by one photon followed by photodetachment of F^- by a second photon.

In contrast to our previous studies of heavy + light-heavy reactions by this method,²¹⁻²³ the FH_2^- photoelectron spectrum does not show any obvious vibrational structure and is therefore difficult to interpret on its own. However, the experimental results can be compared to a recent simulation of the FH_2^- photoelectron spectrum by Zhang and Miller¹⁷ which assumes the T5a potential energy surface for the reaction. This simulation calculates the Franck-Condon overlap as a function of energy between the ground state wave function for FH_2^- (adapted from Ref. 24) and the three dimensional scattering wave functions with total angu-

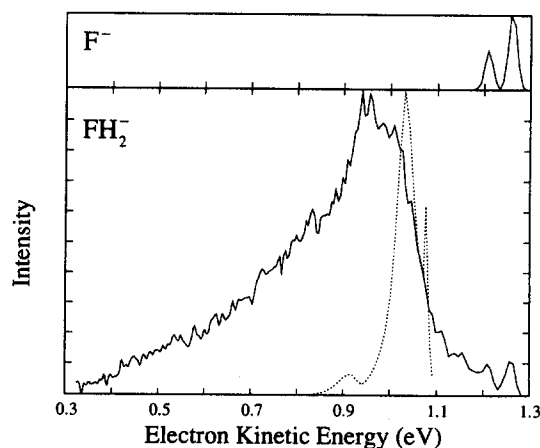


FIG. 1. Experimental (solid) and simulated (dotted, from Ref. 17) photoelectron spectrum of FH_2^- at laser photon energy of 4.66 eV. The simulated spectrum is plotted assuming $D_0 = 0.17$ eV for FH_2^- . Top inset shows photoelectron spectrum of F^- . The two peaks are from transitions to the $^2P_{3/2}$ and $^2P_{1/2}$ states of the F atom.

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lar momentum $J = 0$ supported by the neutral surface. Figure 1 shows there is only limited agreement between the simulated and experimental spectra; they match up well at high electron energy, but the experimental spectrum extends to considerably lower electron energy (higher $E^{(0)}$).

Is the comparison of the experimental and simulated spectra a meaningful diagnostic of the proposed $F + H_2$ potential energy surface? A major advantage of these photodetachment experiments is that since the ions are rotationally cold, it is reasonable to compare a $J = 0$ simulation with experiment. This is in contrast to scattering experiments, simulations of which require a substantially more complex calculation in which one sums over many partial waves. While the photodetachment simulations require an accurate wave function for the ground state of the ion, a good *ab initio* calculation is available in this case. Thus, the disagreement between the experimental and simulated spectra appears, at first glance, to indicate further inadequacies with the T5a potential energy surface.

However, the interaction of F with H_2 leads to three electronic potential energy surfaces.²⁶ While the simulation only considers the ground state surface (the other surfaces correlate adiabatically to highly excited $H + HF$ products), photodetachment of FH_2^- should access the two low-lying excited states as well.²³ The overall width of the experimental spectrum may be due to overlapping transitions to all three surfaces. This possibility must be assessed before drawing any conclusions about what the spectrum tells us about the ground state surface. Approximate calculations of these excited state surfaces have been reported,²⁷⁻³⁰ so it should be possible to simulate the full FH_2^- photoelectron spectrum. We hope the results presented here will stimulate future theoretical work along these lines. In addition to aiding in the interpretation of the FH_2^- photoelectron spectrum, such studies will provide new perspectives on possible nonadiabatic effects in the entrance channel of the $F + H_2$ reaction^{28,30-32} due to the low-lying electronic surfaces.

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